

Carbon Fibers Based on Pyrolytic Lignin

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ABSTRACT: Carbon fibers were prepared from pyrolytic lignin isolated from a commercial bio-oil by thermal spinning followed by carbonization. Compared to other technical lignins, a lower spinning temperature was required for the pyrolytic lignin. The pyrolytic lignins tended to develop fibers with hollow structures and were observed to fuse together during thermostabilization. However, a thermal treatment before fiber spinning was found to maintain the fiber integrity during thermostabilization and the fol-

lowing carbonization process. The mechanical properties and yield of the pyrolytic-lignin-based carbon fiber was found to be comparable to those based on other technical lignins. This work serves as a proof-of-concept study indicating pyrolytic lignin as a potential feedstock for low-cost carbon-fiber production. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: fibers; polyaromatics; renewable resources

INTRODUCTION

The fast pyrolysis of biomass, a zero-waste process, typically generates three products: syngas, bio-oil, and solid char, all of which are potential sources of energy, fuel, and chemicals. However, bio-oil suffers from instability caused by the numerous self-reactions that take place during storage; this affects its ability to be directly used as a fuel in industrial burners and boilers.¹ The likely suspect for this instability is pyrolytic lignin, a highly reactive component that accounts for 20 wt % of bio-oil.² Because of its slower combustion, pyrolytic lignin is also responsible for reducing the combustion efficiency of bio-oil.² Although it is desirable to remove pyrolytic lignin from bio-oil, pyrolytic lignin itself is not used. Removing this component from bio-oil would produce large volumes of waste and, thereby, increase refinement costs. Finding an application for pyrolytic lignin would reduce such costs.

Lignin has been used as a feedstock for carbon-fiber production. The first and only commercially available lignin-based carbon fiber was Kayacarbon, manufactured on a pilot scale by Nippon Kayaku Co. in 1967.^{3–5} These carbon fibers were made from lignosulfonate with poly(vinyl alcohol) added as a plasticizer. Other types of lignin have been investigated as precursors to carbon fibers, including steam

explosion lignin,^{6,7} acetic acid lignin,^{8,9} Alcell lignin,¹⁰ and Kraft lignin.^{10,11} Because of its moderate price, lignin is currently regarded as a potential alternative precursor for carbon-fiber production.¹²

Pyrolytic lignin is similar to other technical lignins in terms of its chemical structure and composition, but it has higher carbon content¹³ and lower average molecular mass.¹⁴ As with petroleum pitch, such characteristics make it an interesting source of carbon fibers because it is known that these aspects facilitate fiber processing (fusion spinning) and increase carbon-fiber yield and, thereby, reduce production costs.¹⁵

In this article, we report the results of a proof-of-concept work in the production of carbon fibers from pyrolytic lignin in terms of its treatments and effects and the characteristics of the resulting carbon fibers.

EXPERIMENTAL

Materials

The source bio-oil, made from mixed hardwood sawdust, was obtained from Dynamotive Energy Systems Corp, Stamford, Connecticut. To prevent side reactions, it was stored at 4°C in the dark.¹³ Organosolv lignin (Alcell) was obtained from Repap Enterprises, Inc., Vancouver, Canada and used as received. Kraft lignin was obtained from MeadWestvaco Corp (Charleston, SC). The Kraft lignin samples were desalted as per our previous work.¹⁰ Specifically, 50 g of Kraft lignin was washed three times with 2 L of distilled water with the pH maintained

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TABLE I
Pyrolytic Lignin Structural Properties

Functional group (mmol/g) ^a			Molecular mass		Thermal analysis	
Aliphatic	Phenolic	Methoxyl	M_w	PDI	T_g (°C)	T_d (°C)
1.7	6.0	2.3	702	2.3	70	150

^a Determined from ¹H-NMR.

below 5 with HCl. The lignin was then air-dried and collected as a fine powder.

Isolation of pyrolytic lignin

Pyrolytic lignin was isolated from bio-oil according to a procedure in the literature.¹³ In a 30-L bucket equipped with an addition funnel, a thermometer, and a homogenizer, 500 mL of bio-oil was added dropwise (~ 10 mL/min) to 15 L of deionized water chilled in an ice-water bath stirred by the homogenizer at 7000 rpm. Phase separation occurred spontaneously upon the introduction of the bio-oil. However, if a greater ratio of oil to water was used, the phase separation of bio-oil droplets could not occur immediately; this led to the conglomeration of bio-oil and, hence, ineffective lignin isolation.

The precipitated lignin was collected by vacuum filtration with Fisherbrand grade P8 qualitative filter paper (Houston, Texas) (cellulose fiber, 24.0 cm in diameter) and was thoroughly washed with 3 L of deionized water. After freeze drying, a light brown fine powder (pyrolytic lignin) was obtained at a yield of 22.3%. The characteristics of the pyrolytic lignin are reported in Table I and were found to be in agreement with literature values.^{2,13}

Preparation methods

A thermal pretreatment was performed in a modified gas chromatography oven (Hewlett Packard HP 5890 series II, Palo Alto, California). Pyrolytic lignin powder (15 g) was placed in a 250-mL, round-bottom flask connected to a vacuum hose. After evacuation of the flask, the temperature was increased at 30°C/min to temperatures ranging from 150 to 180°C followed by isothermal conditions for periods ranging from 0.5 to 6 h. The Alcell lignin and Kraft lignin were both treated at 160°C for 30 min at about 30KPa before fiber spinning as per previous reports.^{10,11}

The spinning apparatus is depicted in Figure 1. Pyrolytic lignin was fed into a hot chamber (zone 1), where it was heated to the predetermined spinning temperature (from 105 to 180°C) and pumped into the spinneret (zone 2), which was also heated at a

predetermined temperature. The resultant extruded lignin fiber was collected on spools by an uptake device (Atlas Electric Devices Co., Chicago, Illinois). Conditions for fiber spinning were set according to literature reports.^{10,11}

Thermostabilization was performed as per the literature¹⁰ with the modified gas chromatography oven. The lignin fibers were heated in air at a rate of 0.5°C/min to 250°C and then held at 250°C for 1 h. Molecular orientation was induced in the fibers through the application of tension to the fibers during the thermostabilization process. The thermostabilized fibers were then carbonized in a GSL1100X tube furnace (manufactured by MTI Corp., Stamford, Connecticut) under nitrogen through heating from 25 to 1000°C at 3°C/min and held for 1 h at 1000°C (the fibers were not under tension because of the limitations of the available carbonization equipments).

We determined the yield after each processing step, except for the spinning yield, by weighing the samples before and after the production step. However, because of the experimental setup, it was not possible to use this protocol to measure the spinning yield; therefore, thermogravimetric analysis (TGA) was employed. In the TGA experiments, the corresponding lignin preparation was first heated to its spinning temperature (zone 1) in 1 min and then heated to the zone-2 spinning temperature in 5 min (estimated residence time) to simulate fiber spinning.

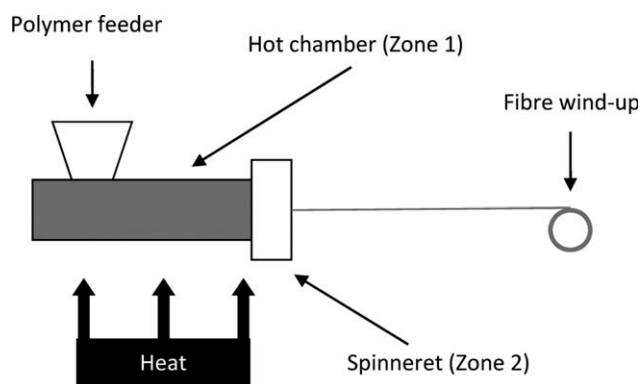


Figure 1 Schematic of the melt-spinning apparatus used to produce the lignin fibers.

Characterization methods

NMR

^1H -NMR and ^{13}C -NMR were measured with a Bruker Avance 300-MHz spectrometer (Billerica, Massachusetts) equipped with a Broadband Observe (BBO) broadband probe. For quantitative ^1H -NMR, 15 mg of acetylated lignin was accurately weighed and dissolved in 0.5 mL of deuterated chloroform. 4-Nitrobenzaldehyde (2 mg) was added to the solution as an internal standard for quantitative determination of functional group content (Table I). The NMR spectra were recorded at 25°C with a 90° pulse width and a 1.3-s acquisition time. A 7-s relaxation delay was used to ensure complete relaxation of the aldehyde protons. A total of 128 scans were collected. Quantitative ^{13}C -NMR spectroscopy was performed with a lignin concentration of 15 wt % in hexadeuterated dimethyl sulfoxide. The sample solutions were filtered before NMR analysis. Relaxation was facilitated by the addition of 10 μL of a chromium acetoacetate solution (final concentration = 10 mM).¹⁶ An inverse gated decoupling pulse program was used with a 90° pulse width, a 0.9-s acquisition time, and a 1.7-s relaxation delay. A total of 80,000 scans were collected. The methoxyl and hydroxyl group contents were calculated from the quantitative ^1H -NMR spectrum of acetylated pyrolytic lignin.

Acetylation was performed by the dissolution of 200 mg of pyrolytic lignin in 8 mL of pyridine/acetic anhydride (1 : 1 v/v) and the stirring of the reaction for 48 h at room temperature. The reaction solution was then added dropwise to 300 mL of stirred ice-water. The precipitated lignin was collected by filtration through a nylon membrane (0.45 μm \times 47 mm) washed with 3 L of ice-cold distilled water and freeze-dried with a VirTis EX freeze dryer (Sacramento, California). Complete acetylation was confirmed by Fourier transform infrared (FTIR) spectroscopy, the results of which are shown in Figure 2. The absence of hydroxyl absorption in the spectrum of the acetylated pyrolytic lignin indicated the complete acetylation of all of the free hydroxyl groups.

Infrared spectroscopy

FTIR analysis was performed with a PerkinElmer Spectrum One FTIR spectrophotometer (Waltham, Massachusetts). The samples were analyzed as films cast on a ZnSn window from a tetrahydrofuran solution (5% w/w).

Elemental analysis

Elemental analysis was performed by the University of British Columbia Mass Spectrometry and Microanalysis Centre with a Carlo Erba elemental analyzer

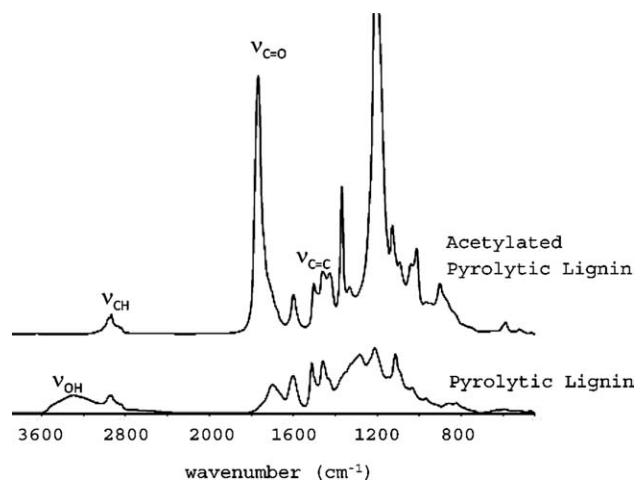


Figure 2 FTIR spectra of the pyrolytic lignin before and after acetylation.

(EA 1108, Lakewood, New Jersey). The C, H, and N contents were determined directly, whereas the O content was calculated by difference.

Gel permeation chromatography (GPC)

The relative average molecular weight distribution of the pyrolytic lignin preparations were determined by GPC (Agilent 1100 UV and refractive-index detectors, Santa Clara, California) with Styragel columns (Styragel HR 4 and HR 2) at 35°C with tetrahydrofuran as the eluting solvent (0.5 mL/min) and UV detection at 280 nm. The pyrolytic lignin concentration was 1 mg/mL, and the injection volume was 100 μL . Polystyrene standards were used for the calibration.

Thermal analyses

TGA was conducted with a TA Q500 TGA instrument. The samples (5–10 mg) were heated from 40 to 1000°C in nitrogen at a heating rate of 20°C/min. The decomposition temperature (T_d) of each of the samples was determined as the temperature at which the sample lost 5% of its weight. The values of T_d are reported as the average of three replicates, with a coefficient of variance of less than 2%.

Differential scanning calorimetry (DSC) measurements were collected with a TA Q1000 DSC instrument. Analyses were conducted under a nitrogen atmosphere with approximately 3 mg of sample in each run. The samples were heated from 20 to 120°C at a heating rate of 10°C/min (first heating run), then cooled to 0°C at 5°C/min (cooling run), and subjected to a second heating from 0 to 200°C (second heating run) at 10°C/min. The glass-transition temperatures (T_g 's) of the samples were

TABLE II
Spinning Temperature and T_g of the Pyrolytic, Alcell, and Kraft Lignins

Lignin type	Spinning temperature (°C) ^a		T_g (°C)	M_w (PDI)
	Zone 1	Zone 2		
Kraft	170	202	131	1256 (2.2)
Alcell	130	158	77	790 (2.5)
Pyrolytic	105	125	70	702 (2.3)

^a The spinning temperature of each type of lignin was recorded when continuous fiber formation was achieved.

measured as the midpoint temperatures of the step changes in heat capacity on the heat-flow curve of the second heating run. Values of T_g are reported as the average of three replicates, with a coefficient of variance of less than 1%.

Scanning electron microscopy (SEM)

Micrographs of gold-coated fibers were taken with a Hitachi S-3000N scanning electron microscope (Tokyo, Japan). The accelerating voltage was 20 kV, and the magnification varied from 100 to 1000 \times .

Tensile strength

The tensile strength, modulus, and elongation of the individual carbon fibers were measured according to ASTM C 1557-03 (2008) with an Instron tension tester (model 5565, Norwood, Massachusetts) with a gauge length of 25 mm. The data are reported as the averages of 20 fibers per sample. The fiber diameters were determined with a calibrated optical microscope and are reported as the average of three measurements along the fiber. The tensile strength and modulus values are reported as the averages plus or minus the 95% confidence interval with a T statistic.

RESULTS AND DISCUSSION

Pretreatment conditions

Pyrolytic lignin, along with Kraft and Alcell lignins, were readily spun into fibers through melt spinning. Table II lists the temperatures required to enable continuous fiber spinning for the first and second heating zones in addition to the corresponding T_g and weight-average molecular weight (M_w) values of the lignin samples. The temperatures required for continuous fiber spinning of the pyrolytic lignin

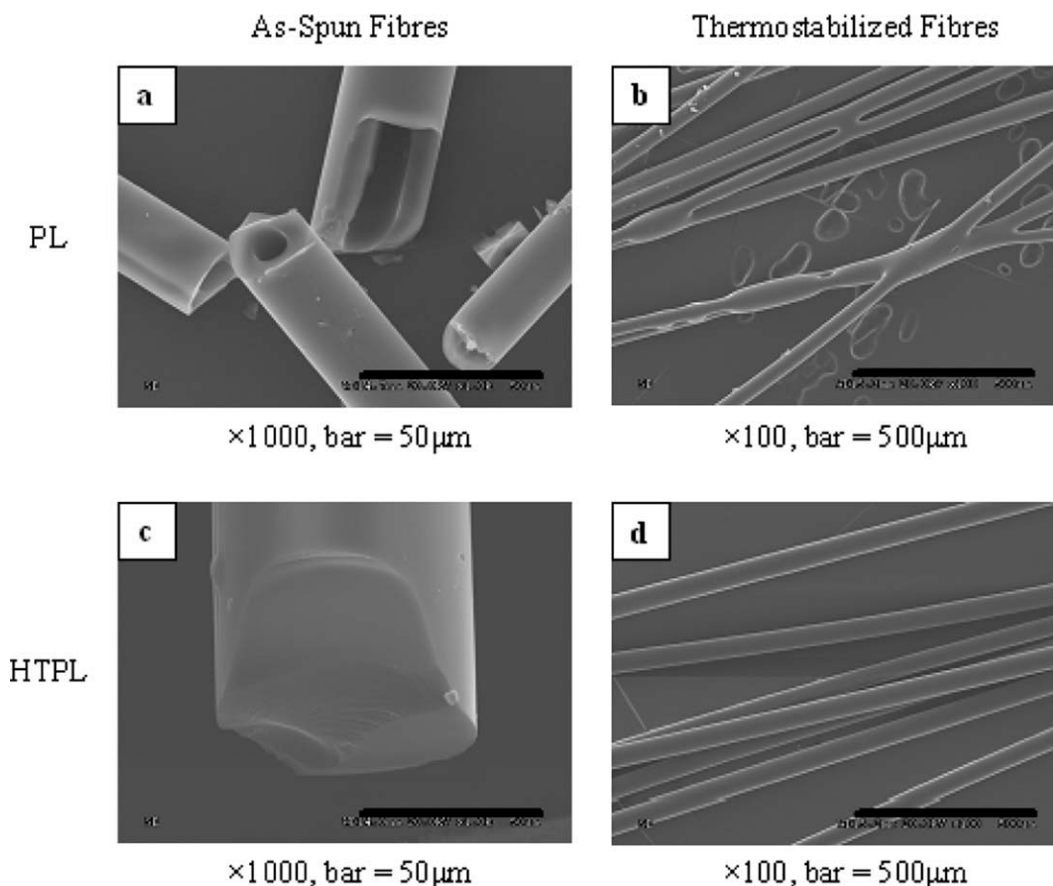


Figure 3 SEM micrographs of (a) PL fibers, (b) thermostabilized PL fibers, (c) heat-treated pyrolytic lignin fibers (HTPL; lignin pretreated at 160°C for 1 h at 30 kPa before spinning), and (d) thermostabilized HTPL fibers.

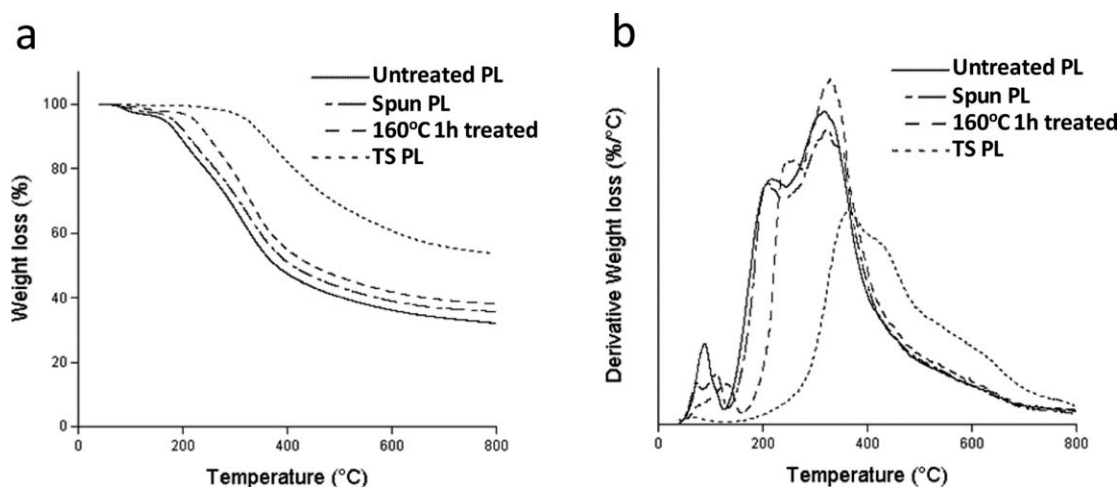


Figure 4 (a) TGA and (b) DTG curves of pyrolytic lignin before (UT PL) and after (spun PL) spinning, pyrolytic lignin after thermostabilization (TS PL), and pyrolytic lignin pretreated at 160°C for 1 h at 30 kPa.

were lower than those needed for both the Kraft and Alcell lignins. The lower spinning temperatures of the pyrolytic lignin were attributed to its lower molecular weight, which was related to an increased free volume and, therefore, a lower T_g .¹⁷ This allowed for a lower softening point.¹⁸

As illustrated in the SEM images in Figure 3, the pyrolytic lignin fibers were porous, an aspect that would significantly impact the mechanical properties of the resultant carbon fiber.¹⁹ These large voids were likely formed during the spinning process as volatile components evolved under the high temperatures of fiber spinning; in fact, during the spinning process, the extruded lignin formed bubbles at the spinneret.

Evidence of volatile components in the pyrolytic lignin was revealed in the subtle changes of the TGA weight loss curve and its derivative thermogravimetry (DTG) curve after fiber spinning (Fig. 4). For the lignin samples before thermostabilization, it was obvious that the major weight loss took place between 200 and 400°C [Fig. 4(a)]. The small peak (corresponding to ~ 4% weight loss) at about 100°C in the DTG curve likely corresponded to the volatile components within the pyrolytic lignin, which after spinning, reduced in intensity and evolved into two peaks: one at about 70°C (2% weight loss) and the other about 110°C (1% weight loss). Similarly, there was a large change in the DTG profile after thermostabilization, during which the pyrolytic lignin was exposed to higher temperatures (250°C) for a longer period of time (1 h) relative to those in the spinning process. Showing less than a 0.3% weight loss, the peak corresponding to volatile components within the pyrolytic lignin almost disappeared after thermostabilization (Fig. 4). There was also an enrichment/enhancement of higher temperatures degrading material at greater than 400°C.

The observed volatile peak at about 100°C might also have been a result of absorbed moisture in the pyrolytic lignin samples. However, the gas chromatographic analysis of these samples (data not shown) indicated the presence of numerous low-molecular-weight volatile compounds, not just water.

Studies of the chemical composition of bio-oil have reported that more than 5 vol % of the bio-oil is various hydrocarbons and other hydrophobic organic molecules,²⁰ which may, after isolation, remain in the water-insoluble fraction of bio-oil (together with pyrolytic lignin). Figure 5 illustrates the ¹³C-NMR spectra of pyrolytic lignin before and after fiber spinning. In addition to the typical lignin aromatic (100–150 ppm), methoxyl (58 ppm), and carbonyl/carboxyl (190–200 ppm) moieties, there was clear evidence of nonaromatic hydrocarbons (10–40 ppm) and oxygenated aliphatic (85–95 ppm) moieties in the pyrolytic lignin.

After fiber spinning, there was little change in the number of peaks, but the relative intensity, or concentration, did not change. The corresponding concentration (integrals) of the various chemical moiety regions for the pyrolytic lignin and as-spun pyrolytic lignin (PL) fibers are listed in Table III. To obtain accurate integrals, 105 mg of lignin was dissolved in 0.5 mL of deuterated dimethyl sulfoxide. All integrals were then normalized against the aromatic region of the untreated (UT) pyrolytic lignin at 6.0 ppm.

The relative intensities of the various carbon signals associated with the aliphatic (10–38 ppm) and oxygenated moieties (58–92 and 170–200 ppm) decreased. Of particular significance were those at 90–92 ppm, oxygenated benzyl carbons and conjugated β oxygenated carbons; 10–25 ppm, terminal methyl groups attached to methylenes, carbonyls (esters), and alkenes; and to a lesser extent, carbons

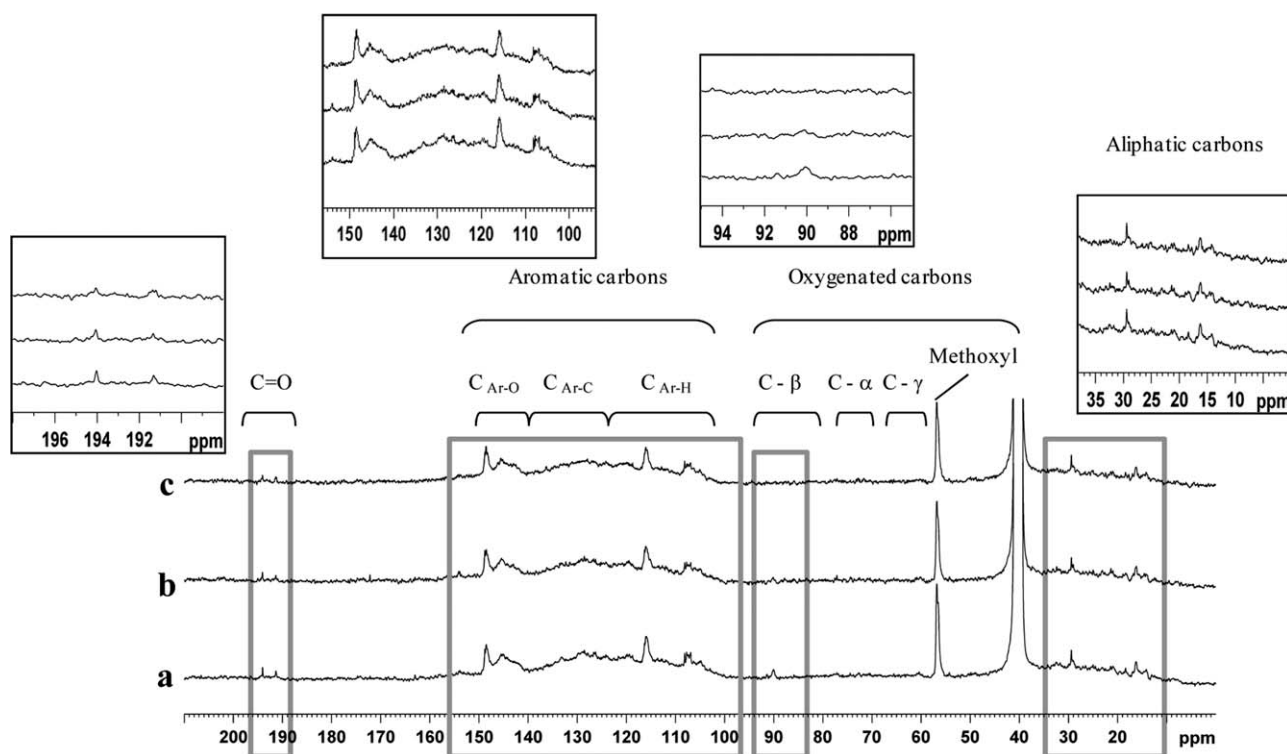


Figure 5 ^{13}C -NMR spectra of UT PL (a) before and (b) after spinning and (c) pyrolytic lignin treated at 160°C for 1 h at 30 kPa.

associated with conjugated carbonyl units (e.g., benzaldehyde) at 191.5 and 194 ppm. Thus, considering the aforementioned observations in the DTG curves [Fig. 4(b)], we concluded that the nonpolar hydrocarbons (corresponding to the region 10–38 ppm) were probably the major source of volatile components in pyrolytic lignin. The relative increase in the integral of the aromatic or alkene region (100–150 ppm) after spinning was probably a result of the partial removal of these volatile compounds.

The relative increase in the concentration of aromatic compounds in the pyrolytic lignin upon thermal treatment (fiber spinning/pretreatment) was also evidenced by elemental analysis. As shown in Table IV, the C/H ratio, an indication of the aromaticity, slightly increased after fiber spinning because of the partial removal of aliphatic hydrocarbons.

The volatile small molecules typically associated with pyrolytic lignin were probably responsible for another problem encountered in the carbon-fiber fabrication from pyrolytic lignin. Figure 3(b) clearly shows that the precursor fibers spun from isolated pyrolytic lignin could not be thermostabilized with the conditions used for other technical lignins (heating rate = $0.5^\circ\text{C}/\text{min}$);^{10,11} the individual fibers that were in contact with each other fused together, even at very low thermostabilization heating rates ($0.1^\circ\text{C}/\text{min}$). As mentioned previously, the pyrolytic lignin used in this study was, in fact, the water-insoluble fraction of bio-oil, and as such, it contained a large number of different hydrocarbons and other hydrophobic organic molecules.²⁰ In addition to their volatility, these small molecules may have acted as plasticizers,²¹ reducing the T_g of the pyrolytic lignin and,

TABLE III
Integral of Various Regions of the ^{13}C -NMR of Pyrolytic Lignin before and after Fiber Spinning and the Pyrolytic Lignin Pretreated at 160°C for 1 h at 30 kPa

	Aliphatic carbon (10–38 ppm)	Oxygenated aliphatic carbon (58–92 ppm)	Aromatic carbon (100–150 ppm)	Carbonyl carbon (170–200 ppm)
Pyrolytic lignin	5.7	2.1	6.0	2.6
PL fibers	4.7	2.0	6.8	2.6
Preheated pyrolytic lignin	3.2	1.9	7.9	2.5

TABLE IV
Elemental Analysis of Pyrolytic Lignin before and after Fiber Spinning and the Pyrolytic Lignin Pretreated at 160°C for 1 h at 30 kPa

	C/H	C (wt %)	H (wt %)	O (wt %)
Pyrolytic lignin	11.43	67.09	5.87	26.66
PL fibers	11.45	67.00	5.85	26.79
Pretreated pyrolytic lignin	11.88	68.34	5.75	25.53

hence, leading to fiber fusing in the thermostabilization process. Unfortunately, because of the chemical changes in the lignins during thermostabilization,²² we were unable to solubilize these fibers and analyze their ¹³C-NMR spectrum.

Despite the good spinning properties of the pyrolytic lignin, a pretreatment to remove volatile components appears necessary to eliminate the large-cavity structures in the PL fibers and ensure that the fibers can survive the subsequent thermostabilization process. In the processing of pitch²³ and other technical lignins^{6–8,10,11,24} to produce carbon fibers, certain modifications or treatments before fiber spinning are typically performed to enhance the material flowability^{6,7} or spinning properties.⁸ On the basis of the DTG curve for the (fused) thermostabilized fibers, a large amount of the pyrolytic lignin material could be removed (degraded) by thermal treatment of the material to temperatures approaching 200°C. Therefore, the pyrolytic lignin was subjected to various temperatures ranging from 150 to 180°C for 0.5–6 h at a reduced pressure of 30 kPa.

GPC analysis of the pyrolytic lignin and the various lignins obtained after heat treatment confirmed

the loss of low-molecular-weight components with increasing temperature [Fig. 6(a)] and time [Fig. 6(b)]. Increasing pretreatment temperature from 150 to 180°C resulted in a significant change in the molecular mass distribution of the pyrolytic lignin [Fig. 6(a)]. The mid-to-low-molecular-mass material seemed to decrease significantly at 150°C; this was accompanied by an increase in higher molecular mass material. This was likely the result of the volatilization of low-molecular-mass components along with some condensation/coupling into larger molecules. Increasing the temperature beyond 150°C led further to an increase in the relative molecular mass distribution, albeit the elution profile was quite similar between treatments.

Almost identical behavior was observed for increasing the time and temperature. Figure 6(b) shows the same decrease in the mid-to-low-molecular-mass material with increasing heating time. However, there appeared to be a more significant increase in the high-molecular-mass material region (2000–7000 Da). In particular, at times of 2 h or greater, the relative average molecular mass distribution contained a significant amount of higher mass material (>2000 Da). This was likely due to enhanced condensation reactions between the various pyrolytic components. The M_w and the polydispersity index (PDI; M_w/M_n , where M_n is the number-average molecular weight) values of these samples are given in Table V.

The pretreatment temperature and time had a similar effect on T_g of the pyrolytic lignin. As shown in Figure 7 and listed in Table V, an increase in the pretreatment time and temperature both resulted in an increase in T_g , which was attributed to both the increase in the molecular weight and the removal of

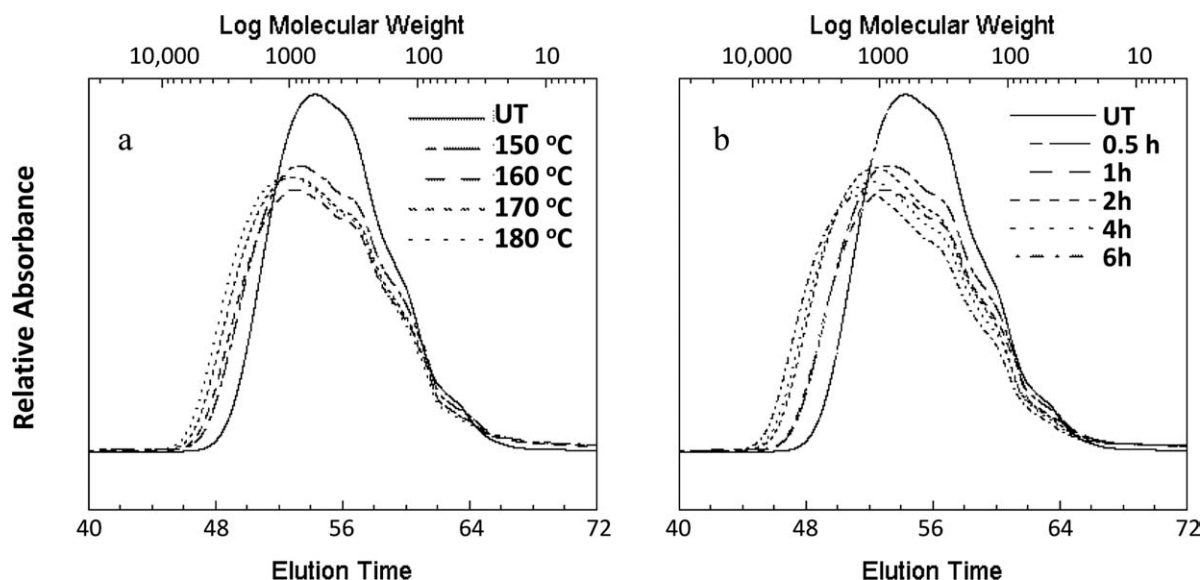


Figure 6 GPC traces for (a) UT and treated pyrolytic lignin for 1 h at various temperatures at 30 kPa and (b) UT and treated pyrolytic lignin treated at 160°C for various periods of time at 30 kPa.

TABLE V
Effect of the Heat-Treatment Temperature and Time on the Molecular Weight and T_g of the Pyrolytic Lignin

Treatment temperature (°C)	Treatment time (h)	M_w	PDI	T_g (°C)
150	1	775	2.9	83.9
160	1	889	3.0	89.1
170	1	925	3.1	97.4
180	1	983	3.0	105.8
160	0.5	862	3.0	83.9
160	2	976	3.3	98.5
160	4	1001	3.3	107.6
160	6	1026	3.6	111.0

low-molecular-mass components, which may have acted as plasticizers.

On the basis of the observations from the GPC and DSC data, the pretreatment time and temperature significantly influenced the molecular weight, thermal properties, and hence, processing properties of the pyrolytic lignin, the effects of which are summarized in Table VI.

Increasing the time or temperature of thermal treatment reduced the maximum speed of spinning. High temperatures and long pretreatment times dramatically reduced the maximum take-up speeds of the resulting pyrolytic lignin (<10 m/min), and continuous fiber spinning was not possible for any prolonged period of time (<1 min maximum). As a result, these preparations were considered not spinnable. At the other extreme, fibers produced from low temperatures and short treatment times fused during the thermostabilization process (marked as F in the table). Only a narrow window of pretreatment conditions was available in which the production of carbon fiber from pyrolytic lignin was possible. Note

that no experimental design was performed to optimize the pretreatment conditions with regard to the mechanical properties of the resulting carbon fibers.

The pretreatment conditions of 160°C and 1 h were chosen to proceed and investigate carbon-fiber production because of its optimum spinning properties. The SEM analyses in Figure 3 reveal a clear improvement in the fiber morphology with the pretreatment. Compared with the fibers spun from untreated pyrolytic lignin [UT PL; Fig. 3(a)], those made from the pretreated pyrolytic lignin [Fig. 3(c)] appeared smooth and continuous with no signs of voids or cavities. Moreover, these fibers could be successfully thermostabilized [Fig. 3(d)].

As expected, the DTG curve [Fig. 4(b)] of the pretreated pyrolytic lignin also changed, similar to that of the spun UT PL, but with a further reduction in the intensity of the volatile peak (showing <3% weight loss). Although not completely removed, as in the DTG curve of thermostabilized UT PL, the volatile components of the pyrolytic lignin were partly removed after the heat treatment. The removal of these volatiles is sufficient and critical in ensuring fiber integrity during thermostabilization with the maintenance of acceptable spinning properties.

Similarly, the ^{13}C -NMR spectrum [Fig. 5(c)] of the pretreated pyrolytic lignin revealed changes in the chemical structure. There was a slight reduction in the methoxyl peak at 57 ppm; this was likely due to demethoxylation reactions.²² Likewise, the peak around 90 ppm, associated with oxygenated aliphatic carbons, diminished completely after the heat treatment.²² A further comparison of the relative integrals for the various regions within the ^{13}C -NMR spectra (Fig. 5) clearly revealed the extent of changes in the pyrolytic lignin as a result of the heat treatment. The pretreated pyrolytic

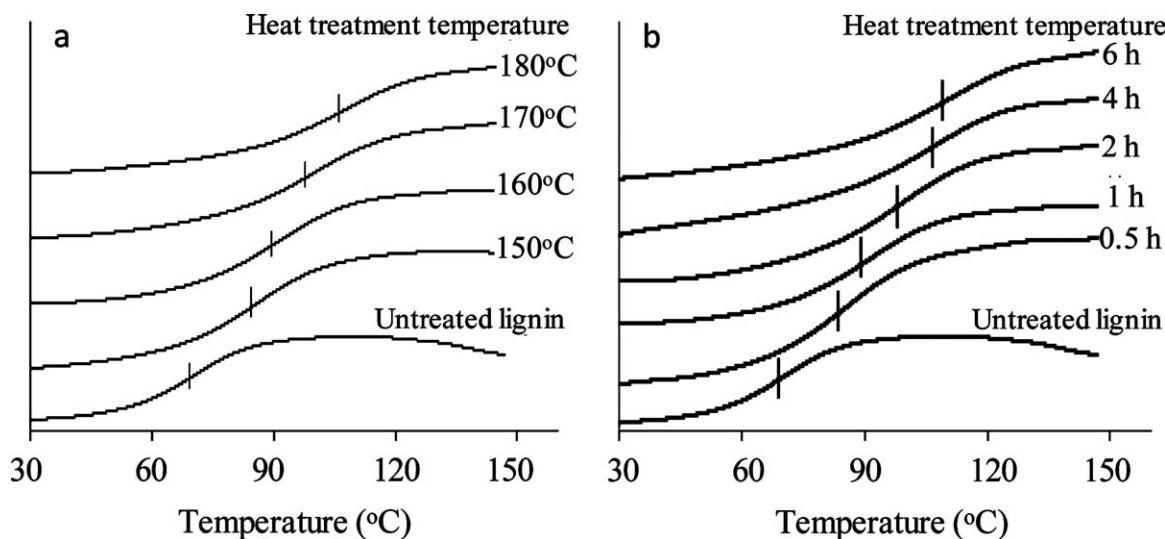


Figure 7 DSC thermograms (exo down) of the UT and pyrolytic lignin treated at (a) various temperatures for 1 h at 30 kPa and (b) 160°C for various periods of time held at 30 kPa.

TABLE VI
Processability of the Pyrolytic Lignins Pretreated under Various Conditions

Treatment temperature (°C)	Time of heat treatment (h)				
	0.5	1	2	4	6
150	F ^a	F ^a	F ^a	S ^b	S ^b
160	F ^a	S ^a	S ^b	S ^b	NS ^c
170	F ^a	S ^a	S ^b	NS ^c	NS ^c
180	F ^b	NS ^c	NS ^c	NS ^c	NS ^c

F, continuous fiber spinning was achieved, and the fibers fused during thermostabilization (0.5°C/min); NS, continuous fiber spinning was not possible; S, continuous fiber spinning was achieved, and the fibers survived thermostabilization (0.5°C/min).

^a Maximum take-up speed \geq 30 m/min.

^b Maximum take-up speed = 10–20 m/min.

^c Maximum take-up speed < 10 m/min.

lignin showed a further decrease in the relative intensity of the carbonyl carbon (170–200 ppm) region and the aliphatic carbon (10–38 ppm) region; again, this supported the removal of the volatile components. As with fiber spinning, the aromaticity, as determined by elemental analysis of C/H (Table IV), showed a further increase after pretreatment; this again corroborated the observations in the ¹³C-NMR spectra.

Carbon-fiber yield and mechanical properties

Yield is an important aspect of the commercial manufacturing of carbon fibers.¹⁰ Lower yields result in higher production costs per unit weight of product. Table VII summarizes the yields of each processing stage in the production of carbon fibers from pyrolytic lignin and Alcell and Kraft lignins.

The thermal pretreatment process had a relatively more pronounced effect on the weight loss of the pyrolytic lignin because the Alcell and Kraft lignin were treated for shorter periods of time, optimized for the substrate.¹⁰ As mentioned previously, the purpose of heat treatment was to remove volatiles from the raw material. Thus, another possible reason for the lower pretreatment yield of the pyrolytic lignin was that it contained more volatiles than the other two types of lignin and, thus, required a longer pretreatment time. This was also the case for isotropic pitch, which had a significantly lower pre-

treatment yield of about 40 wt %, which was attributed to its pretreatment at a relatively high temperature, more than 350°C.²⁵ For all three types of lignin, there was very little yield loss during fiber spinning (<1–4 wt %) and thermostabilization (ca. 4–6 wt %). In contrast, the commercial isotropic pitch increased in weight by 10 wt % after thermostabilization as a result of the oxidation conditions.²⁵

During the carbonization process, most noncarbon elements are removed from the precursor fiber (usually >90 wt %). Because technical lignins have a carbon content of only 59–61 wt %, ¹⁰ the majority of their weight loss occurs in the carbonization step: pyrolytic-lignin-based fibers = 45.0 wt % loss, Kraft lignin \approx 49 wt % loss, and Alcell fibers \approx 54 wt % loss. Here, the slightly higher carbonization yield of the pyrolytic lignin was attributed to its higher carbon content (\sim 67 wt %). In the same way, the isotropic pitch only lost about 20 wt % as a result of the higher carbon content: more than 90 wt %.²⁶ Overall, the total carbon-fiber yields from the Kraft and pyrolytic lignin were found to be higher than that from the Alcell lignin, with pyrolytic lignin having the highest carbon-fiber yield of all three at about 46 wt %. This was significantly higher than that of the isotropic pitch (\sim 33 wt %).²⁵

The ability to stretch the fibers after spinning decreased because of the limitation of the spinning apparatus (inconsistent feeding rate, limited take-up speed, and spinneret size), and the high solidifying speed of lignin as it exited the spinneret. This resulted in carbon fibers from all three lignin types, with diameters ranging from 30 to 50 μ m, that were considerably larger than those of carbon fibers, with diameters of 7–14 μ m, made from other sources.^{7,8} Because the tensile strength of the carbon fibers exhibited significant size dependence, increasing with decreasing fiber diameter,²⁷ it is expected that the mechanical properties will further be enhanced by a decrease in the diameter of the pyrolytic lignin fibers, and this is an area of current research.

The mechanical properties of the pyrolytic-lignin-based carbon fibers fabricated in this study were comparable to those made from other technical lignins¹⁰ (Table VIII). Although carbon fibers with moderate mechanical properties can be made from pyrolytic lignin, their mechanical properties are still

TABLE VII
Comparison of Carbon Fiber Yields from Alcell, Kraft, and Pyrolytic Lignin

Lignin type	Pretreatment (wt %)	Spinning (wt %)	Stabilization (wt %)	Carbonization (wt %)	Overall (wt %)
Kraft	98	98	94	51	46
Alcell	96	99	95	46	42
Pyrolytic lignin	93	96	95	55	46
Isotropic pitch ^a	40	95	110	80	33

^a Values from literature.⁷

TABLE VIII
Comparison of Mechanical Properties of Carbon Fibers
Produced from Alcell, Kraft, and Pyrolytic Lignin

Feedstock material	Diameter (μm)	Modulus (GPa)	Strength (MPa)
Kraft lignin	49 ± 1	41 ± 3	412 ± 39
Alcell lignin	47 ± 2	37 ± 4	379 ± 34
Pyrolytic lignin	49 ± 2	36 ± 1	370 ± 38
Isotropic pitch ^a	8–15	40–50	600–1000

Values are the averages of 20 replicates; deviations are 95% confidence interval based on a *T*-statistic.

^a Values from literature.²⁵

too weak compared to that of the general-performance-grade carbon fibers made from isotropic pitch.

CONCLUSIONS

In the process of carbon-fiber preparation, we employed procedures and conditions similar to those used in the fabrication of carbon fibers based on Kraft and Alcell lignin.^{10,11} It was found that the pretreatment was a critical step in the successful preparation of carbon fibers from pyrolytic lignin. The UT PL tended to develop hollow structures in the process of spinning, and the spun fibers fused together during thermostabilization. Although the hollow-fiber structure may be an advantage in applications where a high surface area is required, it will reduce the strength of the resulting carbon fibers. In fact, fiber fusing during the thermostabilization process may be the biggest concern in the creation of carbon fibers from UT PL. These disadvantages of pyrolytic lignin were effectively eliminated by pretreatment at elevated temperatures under reduced pressure. The temperature and time of pretreatment had strong effects on the carbon-fiber production. Higher temperatures and longer periods of time led to poor fiber spinning of pyrolytic lignin, whereas lower temperatures and shorter times resulted in the lignin fibers fusing together in the subsequent thermostabilization process. Only a narrow window between these two extremes was found to be suitable for carbon-fiber production. Within this window, the pretreatment condition that gave the best spinning

properties was found to be 160°C for 1 h at a 30-kPa reduced pressure. The pyrolytic lignin treated under these conditions produced carbon fibers with mechanical properties and yields comparable to those based on the Kraft and Alcell lignins.

References

- Oasmaa, A.; Kuoppala, E. *Energy Fuels* 2003, 17, 1075.
- Bayerbach, R.; Meier, D. *J Anal Appl Pyrolysis* 2009, 85, 98.
- Fukuoka, Y. *Jpn Chem Q* 1969, 5, 63.
- Mikawa, S. *Chem Economy Eng Rev* 1970, 2, 43.
- Otani, S. *Mol Cryst Liq Cryst* 1981, 63, 249.
- Sudo, K.; Shimizu, K. *J Appl Polym Sci* 1992, 44, 127.
- Sudo, K.; Shimizu, K.; Nakashima, N.; Yokoyama, A. *J Appl Polym Sci* 1993, 48, 1485.
- Uraki, Y.; Kubo, S.; Nigo, N.; Sano, Y.; Sasaya, T. *Holzfor-schung* 1995, 49, 343.
- Kubo, S.; Uraki, Y.; Sano, Y. *Carbon* 1998, 36, 1119.
- Kadla, J. F.; Kubo, S.; Venditti, R. A.; Gilbert, R. D.; Compere, A. L.; Griffith, W. *Carbon* 2002, 40, 2913.
- Kubo, S.; Kadla, J. F. *J Polym Environ* 2005, 13, 97.
- Compere, A. L.; Griffith, W. L.; Leitten, C. F.; Shaffer, J. T. *Adv Affordable Mater Technol* 2001, 33, 1306.
- Scholze, B.; Meier, D. *J Anal Appl Pyrolysis* 2001, 60, 41.
- Scholze, B.; Hanser, C.; Meier, D. *J Anal Appl Pyrolysis* 2001, 58, 387.
- Donnet, J.-B.; Bansal, R. C. *Carbon Fibers*; Marcel Dekker: New York, 1990.
- Capanema, E. A.; Balakshin, M. Y.; Kadla, J. F. *J Agric Food Chem* 2004, 52, 1850.
- Larrain, R.; Tagle, L. H.; Diaz, F. R. *Polym Bull* 1981, 4, 487.
- Brydson, J. A. *Plastics Materials*; Butterworth-Heinemann: Oxford, United Kingdom, 1999.
- Kadla, J. F.; Kubo, S.; Venditti, R. A.; Gilbert, R. D. *J Appl Polym Sci* 2002, 85, 1353.
- Walker, J. C. F. *Primary Wood Processing: Principles and Practice*; Springer: Dordrecht, The Netherlands, 2007.
- Sperling, L. H. *Introduction to Physical Polymer Science*; Wiley-Interscience: Hoboken, NJ, 2005.
- Braun, J. L.; Holtman, K. M.; Kadla, J. F. *Carbon* 2005, 43, 385.
- Morgan, P. E. *Carbon Fibers and Their Composites*; Taylor & Francis: Boca Raton, FL, 2005.
- Kubo, S.; Kadla, J. F. In *Encyclopedia of Chemical Processing*; Lee, S., Ed.; Taylor & Francis: New York, 2006; p 317.
- Bahl, O. P.; Shen, Z.; Lavin, J. G.; Ross, R. A. In *Carbon Fibers*; Donnet, J. B., Wang, T. K., Peng, J. C. M., Rebouillat, S., Eds.; Marcel Dekker: New York, 1998; p 1.
- Alcaniz-Monge, J.; Cazorla-Amoros, D.; Linares-Solano, A. *Fuel* 2001, 80, 41.
- Tagawa, T.; Miyata, T. *Mater Sci Eng A* 1997, 238, 336.